# On the statistical physics of metastable and non-equilibrium stationary states

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The optimization problems defining meta-stable or stationary equilibrium are explored. The Gibbs scheme is modified aiming to describe the statistical properties of a class of non-equilibrium and metastable states. The system is assumed to maximize the usual definition of the Entropy, subject to the standard constant energy and norm restrictions, plus additional constraints. The central assumption is that the existence of the considered metastable state is determined by the action of this additional dynamical constraint, that blocks the evolution of the system up to its maximum Entropy state, thus maintaining it in the metastable or stationary configuration. After requiring from the statistical description to be valid for the combination of two nearly independent subsystems, it follows that the eigenvalues of the constraint operators $C$ should have the restricted homogeneous form $C(p_i) = p_i^q$, in terms of the eigenvalues of the density matrix $p_i$, where $q$ is a fixed real number. Therefore, the distribution of the eigenvalues of the constraint function have the Tsallis structure. This conclusion suggests the interpretation of the $q$ parameter as reflecting the homogeneous dependence of the constraint determining the metastable state on the density matrix. An application to the plasma experiments of Huang and Driscoll is expected to be considered elsewhere in order to compare the results with Tsallis scheme and the minimal Enstrophy one.

## I. INTRODUCTION

The statistical physics of systems which remains for long times in metastable and stationary states is an important theme of research nowadays [2,3,4]. Since the appearance of the proposals for variation of the Boltzman statics proposed by Tsallis for a wide class of non-equilibrium states, it has a been an explosion of interest in the field [1]. A particular point of attention in the literature is devoted to the understanding of the meaning of the special real parameter $q$ which fully characterize the deviation of this new statistical description from the Boltzman one [5,6].

In the present work we explore the statistical properties of metastable and non-equilibrium stationary states with the aim of determining possible new ways of studying these properties and their possible connections with the conceptual elements in the Tsallis approach. Out central starting assumption is that statistical properties differing from those of the Gibbs thermal equilibrium states, could be generated, at least in a large class of systems, by the existence of a dynamically generated constraint stopping for a while their relaxation to the thermal equilibrium, described by the Bloch density matrix. Since the systems under consideration are in quasi-equilibrium in their metastable states, it is here assumed that the additional constraint is approximately conserved. Then, the procedure being proposed here, consists in assuring that the system on its evolution, tends to maximize the usual Entropy in terms of the density matrix $S = -k\ Tr[\rho \log \rho]$, under the standard restrictions of constant energy and norm, plus an additional specially constructed constraint.

The commutation of the statistical density matrix $\rho$ describing the metastable state and the Hamiltonian is assumed since the physical quantities of the metastable state are quasi time independent. Consider now the evolution of the system in the quasi-equilibrium state. It is clear that the probability distribution of the energy values of the Gibbs subsystems will not follow the one given by the Bloch density matrix. There will be a different distribution along the metastable evolution defined by a density matrix $\rho$. This behavior is assumed here to be produced by the existence of a constraint $C$ which constant value during the movement means its conservation. That is, it will be assumed to commute with the Hamiltonian. Also considering that the energy spectrum is non-degenerated, the three operators $H, \rho$ and $C$ can be simultaneously diagonalized. This property allows to express the constraint $C$ as a function of the density matrix $C[\rho]$. Taking into account that the product $C[\rho H$ is also a conserved quantity, a natural way for imposing the effects of the constraint $C$ in the variational Gibbs problem arises: when maximizing the Entropy the constant value of the trace of $C[\rho]H$ will we also required. In other words, this form of the new restriction will added in this paper onto the standard Gibbs maximization problem defining the statistical density matrix by the conditional extremum point of the Entropy as a functional of the density matrix.

As a consequence of the above definitions, the interesting result follows that the additivity of the modified conserved mean values, for two approximately independent subsystems, directly implies that the constraint function $C[\rho]$ should have the Tsallis homogeneous structure $C(\rho) = C_q\rho^q$, with $q$ being an arbitrary real number. The possibility that the density matrices solving the new conditional extremum problem corresponds to metastable states is furnished by the

fact that, by assumption, the constraint $C$ is a weakly conserved quantity, which can be unstable because in general, there could no exist a rigorously conserved dynamical variable associated to it. However, it could has the chance of locally constraint the system for a while, to be in a metastable state.

The equations of the extremum problem for the determination of the density matrix describing the considered metastable or non equilibrium stationary state are also presented.

The work will proceed as follows. In Section 2 the proposal of the scheme is presented. Section 3 is devoted to argue that, if the statistical description of physical system satisfies the additivity condition, then the dependence of the constraint $C$ on the probabilities have the Tsallis structure. The explicit form of the extremum equations determining the density matrix of the metastable state are also presented in this Section. Finally, in the summary, the conclusions are reviewed and some possible extensions of the work commented.

## II. STATISTICAL MECHANICS OF SOME METASTABLE AND STATIONARY STATES

Lets us consider the quantum description of a physical systems having a dynamics fixed by a Hamiltonian operator $H$. In the Gibbs approach the properties of the systems in thermal equilibrium are described by the Bloch density matrix

$$\rho = \exp(-\frac{H}{kT}), \tag{1}$$

satisfying $[H, \rho] = 0$ and which is the conditional maximum of the Entropy functional under constant mean energy. That is, the Bloch density matrix is the extremum of the functional

$$\begin{aligned} S = & -k\ Tr[\rho \log(\rho)] + \alpha(Tr[\rho H] - E) + \\ & + \beta(Tr[\rho] - 1), \end{aligned} \tag{2}$$

in which $\alpha$ and $\beta$ are auxiliary Lagrange multipliers for imposing the conservation of the energy $E$ and the total probability equal to 1, and k is the Boltzman constant.

Let us assume that during a relatively large relaxation time $\tau$, the system is not allowed to approach the thermal equilibrium state, because it is in a metastable or non-equilibrium stationary state. We will assume that this metastable state is produced by a dynamically conserved quantity $C$ which approximately restricts the rapid evolution of the system to the Gibbs thermal equilibrium. The approximate satisfaction of this constraint for large times will be represented here by its, also approximate, commutation with the Hamiltonian.

$$[H, C] = 0.$$

The stationary character of the density matrix $\rho$ will be assumed to also imply $[H, \rho] = 0$. As mentioned above, in order to simplify the discussion, let us consider that the spectrum of the Hamiltonian is not degenerate. Therefore, $H$, $\rho$ and $C$ are all diagonalized in the common basis of eigen-functions of $H$. Henceforth, $C$ can be expressed as a certain function of the density matrix $C = C[\rho]$.

But, due to the above definitions the quantities $C[\rho]H$ is also conserved

$$\begin{aligned} [C[\rho]H, H] &= 0, \\ [C[\rho], H] &= 0. \end{aligned} \tag{3}$$

Therefore, a convenient way emerges for including the effects of the constraint $C$ in the Gibbs maximization problem determining an extremum of the entropy $S$, in the considered metastable or stationary state. The proposal is to include the constancy of the specially defined quantity

$$\frac{Tr[C(\rho)H]}{Tr[C(\rho)]}, \tag{4}$$

through a corresponding Lagrange multiplier in the extremum problem. Then, adding this new constraint to the expression of the Entropy after to be multiplied by the corresponding Lagrange multiplier, the conditional Entropy

functional takes the form

$$
\begin{aligned}
S &= -kTr[\rho\log(\rho)] + \alpha(Tr[\rho H] - E) + \\
&+ \beta(Tr[\rho] - 1) + \gamma(\frac{Tr[C(\rho)H]}{Tr[C(\rho)]} - E_C) \\
&= -k\sum_i p_i \log(p_i) + \alpha(\sum_i p_i\epsilon_i - E) + \beta(\sum_i p_i - 1) + \\
&+ \gamma(\frac{\sum_i C(p_i)\epsilon_i}{\sum_i C(p_i)} - E_F).
\end{aligned} \tag{5}
$$

In what follows we will assume two possibilities:

1) The $\alpha$ parameter is non vanishing and becomes an effective Lagrange multiplier. This corresponds to impose both: the mean energy conservation constraint in common with the $C$ dependent constraint.

2) The $\alpha$ parameter is taken as vanishing and then, it is disregarded as a Lagrange multiplier. This variant corresponds to only fixing the conservation of the new constraint in addition to the constant probability one.

## III. TSALLIS $q$ PARAMETER FROM ADDITIVITY OF THE DESCRIPTION

Let us now consider the implications on the modified problem produced by requiring the additivity of the statistical description. That is, the condition will be imposed that the application of the scheme to a combination of two nearly independent systems, each of them being in the same kind of metastable state, should be equivalent to the separate application to each one of the systems.

Therefore, consider two similar and weakly interacting subsystems, each of them being in a metastable state of the same sort. The Entropy and the constraint functions of the first system after the density matrix furnishing the maximum has been found, are given by

$$
\begin{aligned}
S^{(1)} &= -k\sum_i p_i^{(1)} \log(p_i^{(1)}), \\
E^{(1)} &= \sum_i p_i^{(1)}\epsilon_i^{(1)}, \quad 1 = \sum_i p_i^{(1)}, \\
E_C^{(1)} &= \frac{\sum_i C(p_i^{(1)})\epsilon_i^{(1)}}{\sum_i C(p_i^{(1)})]}.
\end{aligned} \tag{6}
$$

Analogously for the second system, these same quantities take the form

$$
\begin{aligned}
S^{(2)} &= -k\ \sum_i p_i^{(2)} Log(p_i^{(2)}), \\
E^{(2)} &= \sum_i p_i^{(2)}\epsilon_i^{(2)}, \quad 1 = \sum_i p_i^{(2)}, \\
E_C^{(2)} &= \frac{\sum_i C(p_i^{(2)})\epsilon_i^{(2)}}{\sum_i C(p_i^{(2)})]}.
\end{aligned} \tag{7}
$$

The description is assumed to be also valid for the combined system. In this case the Entropy and constraints for the composite body are

$$
\begin{aligned}
S^{(1,2)} &= -k\sum_{(i,j)} p_{(i,j)}^{(1,2)} \log(p_{(i,j)}^{(1,2)}), \\
E^{(1,2)} &= \sum_{(i,j)} p_{(i,j)}^{(1,2)}\epsilon_{(i,j)}^{(1,2)}, \quad 1 = \sum_{(i,j)} p_{(i,j)}^{(1,2)}, \\
E_C^{(1,2)} &= \frac{\sum_{(i,j)} C(p_{(i,j)}^{(1,2)})\epsilon_{(i,j)}^{(1,2)}}{\sum_{(i,j)} C(p_{(i,j)}^{(1,2)})},
\end{aligned} \tag{8}
$$

where $(i,j)$ symbolizes the couple of indices defining the states of the combined system $|i,j\rangle = |i\rangle \times |j\rangle$. Then, the independence of the systems allows to write for the probability of the combined state $|i,j\rangle$ the relations

$$\begin{aligned} p^{(1,2)}_{(i,j)} &= p^{(1)}_i p^{(2)}_j, \\ \sum_{(i,j)} p^{(1)}_i p^{(2)}_j &= \sum_i p^{(1)}_i \sum_j p^{(2)}_j = 1. \end{aligned} \tag{9}$$

Therefore, the constant probability constraint of the individual components imply the same property for the combined system.

The additivity of the Entropies follows in similar way as usual

$$\begin{aligned} S^{(1,2)} &= -k \sum_{(i,j)} p^{(1,2)}_{(i,j)} \log(p^{(1,2)}_{(i,j)}) \\ &= -k \sum_{(i,j)} p^{(1)}_i p^{(2)}_j \log(p^{(1)}_i p^{(2)}_j) \\ &= -k \sum_i p^{(1)}_i \log(p^{(1)}_i) - k \sum_j p^{(2)}_j \log(p^{(2)}_j) \\ &= S^{(1)} + S^{(2)}, \end{aligned} \tag{10}$$

as well as the addition of the mean energies

$$\begin{aligned} E^{(1,2)} &= \sum_{(i,j)} p^{(1,2)}_{(i,j)} \epsilon^{(1,2)}_{(i,j)}, \\ &= \sum_{(i,j)} p^{(1)}_i p^{(2)}_j (\epsilon^{(1)}_i + \epsilon^{(2)}_j) \\ &= \sum_{(i,j)} p^{(1)}_i p^{(2)}_j \epsilon^{(1)}_i + \sum_{(i,j)} p^{(1)}_i p^{(2)}_j \epsilon^{(2)}_j \\ &= \sum_i p^{(1)}_i \epsilon^{(1)}_i + \sum_j p^{(2)}_j \epsilon^{(2)}_j \\ &= E^{(1)} + E^{(2)}. \end{aligned}$$

Now, we will also assume that the modified $C$ dependent mean value also satisfies the statistical independence condition for the combined system

$$C^{(1,2)}_{(i,j)} = C^{(1)}_i C^{(2)}_j. \tag{11}$$

where $C^{(1,2)}_{(i,j)} = C(p^{(1,2)}_{(i,j)})$, $C^{(1)}_i = C(p^{(1)}_i)$ and $C^{(2)}_i = C(p^{(2)}_i)$. Therefore, the specially defined mean value also satisfies the additivity properties as follows

$$\begin{aligned} E^{(1,2)}_C &= \frac{\sum_{(i,j)} C^{(1,2)}_{(i,j)} \epsilon^{(1,2)}_{(i,j)}}{\sum_{(i,j)} C^{(1,2)}_{(i,j)}}, \\ &= \frac{\sum_{(i,j)} C^{(1)}_i C^{(2)}_j (\epsilon^{(1)}_i + \epsilon^{(2)}_j)}{\sum_{(i,j)} C^{(1)}_i C^{(2)}_j} \\ &= \frac{\sum_{(i,j)} C^{(1)}_i C^{(2)}_j \epsilon^{(1)}_i}{\sum_{(i,j)} C^{(1)}_i C^{(2)}_j} + \frac{\sum_{(i,j)} C^{(1)}_i C^{(2)}_j \epsilon^{(2)}_j}{\sum_{(i,j)} C^{(1)}_i C^{(2)}_j} \\ &= \frac{\sum_i C^{(1)}_i \epsilon^{(1)}_i}{\sum_i C^{(1)}_i} + \frac{\sum_j C^{(2)}_j \epsilon^{(2)}_j}{\sum_i C^{(1)}_i} \\ &= E^{(1)}_C + E^{(2)}_C. \end{aligned} \tag{12}$$

However, this condition also imposes a strong restriction on the possible forms of the function $C$ defining the modified mean value. In order to see this, the statistical independence condition (11) can be rewritten in the form

$$C(p_i^{(1)}p_j^{(2)}) = C(p_i^{(1)})C(p_j^{(2)}). \tag{13}$$

Considering $C$ as expanded in powers

$$C(x) = x^\nu \sum_{n=0}^{\infty} f_n \; x^n \tag{14}$$

and substituting this relation in (13), it follows

$$(p_i^{(1)}p_j^{(2)})^\nu \sum_{n=0}^{\infty} f_n(\; p_i^{(1)})^n(\; p_j^{(2)})^n = (p_i^{(1)})^\nu(p_j^{(2)})^\nu \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} f_n f_m(\; p_i^{(1)})^n(\; p_i^{(2)})^m,$$

which after cancelling the common factors can be rewritten as

$$0 = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} f_n(\; p_i^{(1)})^n(\; p_i^{(2)})^m(\delta_{nm} - f_m). \tag{15}$$

Next , after taking into account the completeness of the basis of powers of the variables, and assuming that the values of the $p_i$ variables form a continuous for all values of $i$, it follows

$$f_n(\delta_{nm} - f_m) = 0, \quad \text{for all} \;\; m \text{ and } n \; . \tag{16}$$

Henceforth, assuming that a particular $f_{m_o} \neq 0$, implies that for all $m \neq m_o$ the $f_m$ expansion parameters are equal to zero. Thus, the only non-vanishing coefficient is the $f_{m_o}$.one. Consequently, the allowed forms of $C$ are

$$\begin{aligned} C(\rho) &= f_{m_o}\rho^{m_o+\nu} \\ &= f_q \; \rho^q. \end{aligned} \tag{17}$$

### A. Extremum equations

After the form of the function $C$ has been determined, the Entropy functional as modified to impose the constraints through the Lagrange multipliers procedure, can be written in the more explicit form

$$\begin{aligned} S = &-k\sum_i p_i \log(p_i) + \alpha(\sum_i p_i\epsilon_i - E) + \beta(\sum_i p_i - 1) + \\ &+ \gamma(\frac{\sum_i p_i^q \epsilon_i}{\sum_i p_i^q} - E_q). \end{aligned} \tag{18}$$

where the index $C$ in $E_F$ has been changed to $q$ .

The extremum equations are

$$\begin{aligned} &\frac{\partial S}{\partial p_i} = 0, \quad \frac{\partial S}{\partial \alpha} = 0, \quad i = 1, 2...\infty \\ &\frac{\partial S}{\partial \beta} = 0, \quad \frac{\partial S}{\partial \gamma} = 0, \end{aligned} \tag{19}$$

which after their explicit evaluation leads to the following set of coupled equations for the eigenvalues of the density matrix $\rho$

$$\begin{aligned} k - \alpha\; \epsilon_i - \beta &= -k\log(p_i) + \gamma\frac{q\; p_i^{q-1}}{\sum_i p_i^q}(\epsilon_i - E_q), \\ E &= \sum_i p_i\epsilon_i, \\ 1 &= \sum_i p_i, \\ E_q &= \frac{\sum_i p_i^q \epsilon_i}{\sum_i p_i^q}. \end{aligned} \tag{20}$$

Multiplying the first equation by $p_i$ and summing over $i$, a relation between the Entropy and the lagrange multipliers follows

$$
\begin{aligned}
0 &= -k \sum_i p_i \log(p_i) + \gamma \sum_i \frac{q\ p_i^q}{\sum_i p_i^q}(\epsilon_i - E_q) - 1 + \alpha E + \beta, \\
&= -k \sum_i p_i \log(p_i) - k + \alpha E + \beta \\
&= S + \alpha E - k + \beta. \qquad (21)
\end{aligned}
$$

As usual it could be employed for constructing a generalization of the Free Energy and other Thermodynamical Potentials. However, we will delay this discussion to future extensions of the work.

## IV. SUMMARY

A statistical description of metastable states is proposed. The main idea is that a large class of metastable and stationary states could be associated to the existence of quasi-conserved constraints blocking the approach of the system to thermal equilibrium. Assuming that this is the case, it is shown that if the statistical properties of the system have the additivity property, the eigenvalues of the constraint function in terms of the probabilities have the Tsallis structure $p_i^q$. This outcome indicates the interpretation of the Tsallis parameter as furnishing the degree of homogeneity of the constraint as a function of the density matrix. Finally, the proposed description is defined by the density matrix which maximizes the usual expression of the Entropy under the conservation of the mean energy, normalization and the additional constraint assumed to be enforcing the metastable state.

In future extensions of the work, it is planned to determine the predictions of the analysis for the plasma experiments of Huang and Driscoll [3]. It is expected that the procedure could appropriately describe the experimental results of Ref. [3]. Those results were reasonably explained by the minimization of the so-called Enstrophy function [3] and also by a study employing the Tsallis statistics in Ref. [2]. Thus, the consideration of this task seems to be an appropriate step in checking the predictions of the discussion presented here.

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